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Abraham model linear free energy relationships for describing the partitioning and solubility behavior of nonelectrolyte organic solutes dissolved in pyridine at 298.15 K

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ABSTRACT

A headspace gas chromatographic method is used to measure infinite dilution activity coefficients of 20 liquid organic solutes dissolved in pyridine at 298.15 K. The measured infinite dilution activity coefficients are used to calculate air-to-pyridine and water-to-pyridine partition coefficients. The calculated partition coefficients, combined with published experimental data for an additional 52 inorganic and organic solutes taken from the chemical literature, are used to derive Abraham model correlations for describing the transfer of nonelectrolyte solutes into pyridine from both water and the gas phase. The derived mathematical described the air-to-pyridine and water-to-pyridine partition coefficients to within 0.13 log units.

1. Introduction

Selection of the most suitable organic solvent for an industrial manufacturing process is a critical task as one must consider not only the physical and chemical properties of the potential solvent candidates, but economical and safety issues as well. Physical properties, such as density and viscosity, have been measured for most of the commonly used organic solvents. For mixed solvent systems predictive methods have been developed for estimating densities and viscosities using group contribution methods if actual experimental values are not available. Experimental data is less abundant for solvent properties involving the solubilization of organic and inorganic solute molecules. There are several millions of known organic and inorganic compounds, and it is not feasible to perform solubility measurements for every possible solute-solvent pair. Fortunately predictive methods are also available for estimating the solubility of gaseous, liquid and crystalline nonelectrolyte solutes dissolved in neat organic solvents and multicomponent organic solvent mixtures. The "quality" of the predicted values ranges anywhere from "very good" to "marginal" depending upon the complexity of the solute and solvent molecules being considered. Very good predictions are often obtained for very simple solute-solvent systems containing only nonspecific interactions. The more complex systems involving multi-functional solute and solvent molecules, however, present greater challenges. These latter systems may involve formation of solute-solute, solvent-solvent and/or solute-solvent association complexes through the formation of hydrogen-bonds.

Our contribution in the area of solvent selection has been twofold. First we have experimentally determined infinite dilution activity coefficients [1–9], air-to-liquid partition coefficients [1–9] and solubility data [3–6] for solutes dissolved in wide range of organic solvents of varying polarity and hydrogen-bonding character. The published experimental data is available to the scientific community for utilization in the development of better predictive models. Concurrent with our experimental endeavors we have been very active in developing mathematical expressions for predicting the fore-mentioned solute transfer properties in more than 100 neat organic solvents [3–6,10], in more than 70 different

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